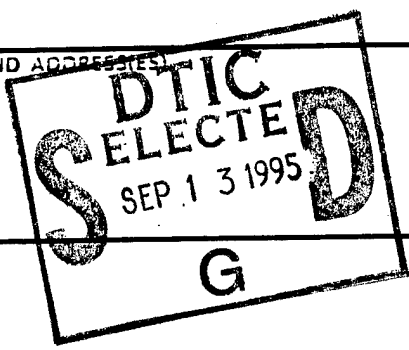


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Near-IR Spectra of Polyethylene, Polyethylene Glycol and Polyvinylethyl Ether

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Abstract

The near-IR spectrum of polyethylene, polyethylene glycol and polyvinylethyl ether have been measured. The CH and OH stretch and bend absorptions have been assigned using local mode theory. The CH stretch anharmonicities are about 57 cm^{-1} , typical of CH anharmonicities in molecular samples. The CH bend anharmonicities are 7, 10 and 11 cm^{-1} , respectively, for polyethylene, polyethylene glycol and polyvinylethyl ether. The CH bend absorption intensities decrease by about a factor of 4 allowing these bending transitions to be observed up to the fourth overtone transition.

Introduction

IR spectroscopy is a powerful method of analysis in polymer science¹. The utility of IR spectra arises from the specific absorption frequencies of chemical functional groups. The functional group specificity is a tool in understanding progress in polymerization, structure of polymers, presence of impurities and stability of polymer blends. IR spectroscopy is not only qualitative but quantitative. However, the high IR absorptivity of polymer materials can lead to the problem of saturation, especially in the CH stretch regions. IR spectral techniques for polymers must contend with the low throughput which sometimes limits the usable spectral range.

The vibrational absorptions in the IR are attributed to transitions from $v=0$ to $v=1$ for the normal modes in the material. The strongest absorption features belong to transitions for modes with the largest change in the dipole moment. Due to the myriad of vibrational motions, many transitions are possible. In theory the more transitions observed the more structural information obtained. In practice, however, the vibrational bands overlap one another defying analysis. For example, all the C-C stretches and C-H deformations which are of importance in polymer diagnosis fall within a narrow region between 1000 to 1600 cm^{-1} . Broadening of the bands by the polymer environment exacerbates the problem.

The first overtone spectra in the near IR have been used to some extent in polymer analysis.² However, the frequencies and intensities are quite sensitive to the molecular environment², discouraging the use of near-IR in polymer science due to the difficulty in assigning the vibrational bands. As a consequence only first overtone spectra have been used

successfully since the first CH stretch can be identified as approximately twice the fundamental wavenumber.

The work presented in this paper indicates that local mode theory of vibrational overtone absorptions in gases and liquids^{3,4} can be applied to polymer systems. Measurements of the frequencies, anharmonicities and intensities can be used to characterize the structure of the polymer molecules. Overtone spectroscopy monitors the vibrational motion of particular bonds called local modes⁵. The transition energies of a particular local mode can be described by the following formula

$$\Delta E = (w_e - w_e x_e) v - w_e x_e v^2 \quad 1.$$

where v is the vibrational quantum number, w_e is the mechanical frequency and $w_e x_e$ is the anharmonicity. Overtone spectra easily distinguish olefinic from methylenic CH absorptions⁶. Only those vibrations with large anharmonicities absorb near-IR and visible light so the deformations, torsions, CC stretches, which complicate the assignments in IR spectra, are not observed. The pure bending absorptions are not directly seen in overtone spectra but are observed as they couple to the CH stretch.^{6a} These absorptions are characteristic of the chemical environment, similar to IR absorptions, except that the spectral shift is much larger due to the anharmonicity. Typical CH stretch anharmonicities for gaseous alkanes and alkenes range from 56 to 65 cm^{-1} .³ For example, CH stretches belonging to axial or equatorial bonds in cyclohexane are easily distinguished³. The gauche and trans OH can be identified in alcohols⁷ and the in plane methyl CH bonds absorb at a different frequency than the out of plane ones, e.g. in methylcyclopentadiene⁸. In addition the position of the NH overtones has been investigated in primary⁹ and cyclic amines¹⁰. In comparison to this work each type of inequivalent CH, NH and OH bond in the polymer should also absorb a characteristic frequency of light.

There are a few literature examples which document the usefulness of overtone spectra in macromolecules. Manzanares¹¹ studied *cis*-1,4-polybutadiene in CCl_4 and obtained a very simple overtone spectrum in the $\Delta v = 3$ and 4 region of the CH stretch. The spectra at each overtone level possess three peaks which are assigned by comparison to the overtone spectra of liquid *cis* and *trans*-hexene. The most intense peak corresponds to the olefinic CH stretch absorption while Manzanares suggests that the other two arise from the pseudo-axial and equatorial CH bonds. This study indicates that specific information about the structure of polymers can easily be obtained from vibrational overtone spectroscopy and that the rules which apply in gaseous spectra transfer directly into the polymer spectra.

Higher overtone spectroscopy does not suffer from saturation effects so that bulk samples can be analyzed without special preparation. The sensitivity of near-IR absorptions to molecular environment can be used to monitor the effects of polymerization on various bonds within the

monomer. Furthermore, the large anharmonicities serve to separate the peaks corresponding to CH bonds at different positions along the polymer.

Experimental

The spectra were recorded on a Mattson FT Near-IR spectrometer with a tungsten lamp, quartz beam splitter and a PdSe detector. Most of the spectra were taken with at least 50 scans. The polyethylene was a film sample. In order to increase the absorbance at the higher energies as many as 14 thicknesses of the sample were used. The polyethylene glycol and polyvinylethyl ether were dissolved in CCl_4 . The concentration was increased to obtain the higher overtone spectra. The spectra in the mid IR were obtained on a Mattson FTIR. All spectra were recorded at 1 cm^{-1} resolution.

Results and Discussion

The vibrational spectra of polyethylene, polyethylene glycol and polyvinylethyl ether are shown in figures 1, 2 and 3, respectively. The spectra are shown with the absorbance scale for the lower trace, however peaks at the higher energy portion of the wavenumber scale are enlarged. These high energy spectra were obtained using concentrated samples which were saturated at the low energy portion of the scale.

The peak wavenumbers are tabulated in Table 1. Assignments were guided by Birge-Sponer plots of $\Delta E / \nu$ plotted against ν , according to equation 1. The reasoning behind these assignments is explained in the following paragraphs.

Polyethylene

Figure 1 presents the vibrational spectrum of polyethylene. The CH stretch overtones are clearly observed. In the CH fundamental region two strong peaks, separated by about 37 cm^{-1} , appear. The first overtone of these absorptions occur at 5664 and 5774 cm^{-1} but are now separated by 112 cm^{-1} . By the $\nu = 3$ and 4 CH overtones only one absorption feature with a symmetric band shape appears. At these high vibrational energies the CH oscillators are behaving in a local mode fashion. Using the lower of the two transition wavenumbers for $\nu=1$ and 2 and the peak wavenumbers for the single peaks at $\nu=3$ and 4, a Birge-Sponer plot indicates that the anharmonicity for the CH stretch in this polymer is 57 cm^{-1} , similar to those found in molecular spectra. In polyethylene only one type of CH oscillator occurs so the simple vibrational progression of this oscillator confirms the existence of the local mode for this polymer.

The comparison to molecular spectra breaks down however in assigning some of the other peaks in the spectrum. We believe that the transitions at 4322 and 7175 cm^{-1} arise from the

CH bend whose fundamental is observed at 1464 cm^{-1} . The bending transitions also contribute to the absorptions at 2899 and 5776 cm^{-1} however the assignment is difficult to make because of the overlap with the CH stretch. These bending transitions are observed through the $v = 5$ level. Pure bending transitions of this type are rarely seen in molecular spectra^{3, 4, 5}. The anharmonicity for the bend is 7 cm^{-1} using the transition energies corresponding to the $v=1, 2, 3, 4$ and 5 transitions in the Birge-Sponer plot.

In this spectrum the CH stretch motion is relatively unchanged going from a monomer to a polymer environment, however the bend motion is more anharmonic. For example, the CH stretch frequencies for various deuterated derivatives of propane and butane have first overtones ranging from 5673 to 5781 cm^{-1} and second overtones ranging from 8246 to 8495 cm^{-1} .¹² The corresponding absorptions in the polyethylene fall in the same range. The bending absorptions in polyethylene are strong relative to those in the monomer and can be observed in the overtone spectrum up to the fourth overtone transition.

Polyethylene glycol

Figure 2 shows the vibrational spectrum of polyethylene glycol dissolved in carbon tetrachloride. This overtone spectrum should involve two types of CH stretches and the OH stretch oscillators. Of these two the OH is easy to identify as the first overtone absorption at 7030 cm^{-1} . For the fundamental there are two choices, either 3575 or 3500 cm^{-1} . The Birge-Sponer plot identifies the absorption at 3575 cm^{-1} as the OH stretch fundamental with an anharmonicity of 60 cm^{-1} for this stretch. The absorption at 3500 cm^{-1} must be a combination band. The CH absorptions are more difficult to identify because they are overlapped by the CH bend overtone. A process of elimination can be used wherein the bends are identified first and then the CH stretches.

The second and third overtones of the CH bends are the prominent bands at 4331 and 5761 cm^{-1} . This indicates that the band to the blue of the CH stretch fundamental at 2934 cm^{-1} must be the first overtone of the CH bend. Using the fundamental absorption at 1470 cm^{-1} with these three peaks in a Birge-Sponer plot yields an anharmonicity for this bend of 11 cm^{-1} . The OH bend must lie lower in frequency than the CH bend. The prominent bands at 4006 and 5173 cm^{-1} most likely belong to the OH bend. The fourth overtone absorption is a weaker band at 6390 cm^{-1} . Using these three members of the progression yields an anharmonicity of 19 cm^{-1} which is high for a bending mode. The absorption at 5173 cm^{-1} is probably overlapped with other combination overtones which appear to shift its maximum to the red.

The above assignments leave the peak at 5555 cm^{-1} as the CH stretch overtone. Two types of CH stretches cannot be identified in the overtone region for this polymer. Perhaps at the second overtone the different CH overtones can be identified.

Polyvinylethyl ether

In polyvinylethyl ether (figure 3) there are four types of inequivalent CH oscillators so the CH stretching overtone spectrum is complicated. In the fundamental region three CH stretch absorptions are observed. The first overtone of the CH stretch is a broad peak at 5763 cm^{-1} with shoulders to the high and low energy side. The second overtone absorption is also broad with a peak intensity at 8440 cm^{-1} and a shoulder to the red at 8150 cm^{-1} . Using these peaks and the central CH fundamental at 2928 cm^{-1} in a Birge-Sponer fit yields an anharmonicity of 57 cm^{-1} .

The pure bending absorptions are easily assigned to the 4334 and 7103 cm^{-1} absorptions which indicate a 10 cm^{-1} anharmonicity for this motion. The bend overtones also fall in the CH stretch regions further complicating these band contours.

Intensities

The integrated intensities for molecular overtone spectra decrease with increasing quantum level. This is also true for these polymer samples. The most noticeable difference is that the strength of the CH bend intensities does not fall off as quickly as in molecular spectra allowing the higher CH bend overtones to be identified. The relative intensity of the CH bend absorptions in polyethylene was determined experimentally by integrating the fundamental and fourth overtone CH bend peaks. These peaks were chosen for their simple band contours with no overlap due to other bending/stretching modes. The peaks showed an intensity drop-off of about a factor of 4 with each quantum level, much less than the tenfold decrease observed in molecular spectra.

Conclusion

The vibrational overtone spectra of three polymeric samples have been recorded in the near-IR spectral range and the observed peaks assigned according to the local mode model. Overtone transitions of the CH and OH stretches as well as the CH and OH bends have been identified. The largest difference between the polymer overtone spectra and those of molecular samples is the strength of the bending absorptions. Overtones of the pure bending motion are seen up to the fourth overtone transition.

Acknowledgements

This work was supported in part by the Office of Naval Research.

Table 1 Vibrational Transitions (in wavenumbers, cm^{-1}) and Assignments for Polyethylene, Polyethylene glycol and Polyvinylethyl ether

	Polyethylene	Polyethylene Glycol	Polyvinylethyl ether
OH bend		1351	
	1303 1377		
CH bend	1464	1470	1456
		2856	2870
CH stretch	2855 2899	2885	2928
CH bend $\nu=2$		2934	2974
OH stretch		3500 3575	
		3630	
OH bend $\nu=3$		4006	
CH bend $\nu=3$	4251 4322	4331	4058 4334
OH bend $\nu=4$		4872 5173	5286
CH stretch $\nu=2$	5664	(5555 and 5761)	5763
CH bend $\nu=4$	5776	5761	
			5901
OH bend $\nu=5$		6390	
CH bend $\nu=5$	7175		7091
OH stretch $\nu=2$		7030	8150
CH stretch $\nu=3$	8243		8440
CH stretch $\nu=4$	10778		

Table 2 Anharmonicities (in wavenumbers, cm^{-1}) for Polyethylene, Polyethylene Glycol and Polyvinylethylene Ether

	CH stretch	CH bend	OH stretch	OH bend
Polyethylene	57	7		
Polyethylene Glycol	-	11	60	19
Polyvinylethyl Ether	57	10		

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Figure Captions

1. Vibrational spectrum of polyethylene - The absorbance scale belongs to the lowest trace. The other traces have been expanded to reveal the weak absorption features.
2. Vibrational spectrum of polyethylene glycol - The absorbance scales for each trace are arbitrarily expanded to reveal the weak absorption features.
3. Vibrational spectrum of polyvinylethyl ether - The absorbance scales for each trace are arbitrarily expanded to reveal the weak absorption features.

